Relative Viscosity and Concentration

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With 13 figures and 1 table

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Introduction

A survey and discussion is given of the equations which have been proposed for describing the relation between relative viscosity of disperse systems and concentration of the dispersed phase. These formulas have been given originally mostly for some specific type of dispersion, such as suspensions of uniform rigid spheres, polymer solutions of one type or another, "colloidal" solutions, or for some restricted range of concentration, and of the shear rate. For almost all these very many and varying formulas experimental proof has been advanced by the authors.

Some equations have been developed on a theoretical foundation, taking into account mechanical, geometric, stereometric, and hydrodynamic considerations, reckoning with the effect of perturbations, collisions, doublet-, multiplet-, chain-formation. Screening and caging factors are proposed. Rotations and translations are discussed, diffusion processes are treated. One viscosity theory is based on transport phenomena, treated as rate processes. Attraction and repulsion forces between particles and particles and medium, of electrical and other types are introduced. Several theories for structure forming are given, considering the disperse system e. g. as a loose network with temporary junctions.

Other formulas may be called half-theoretical. A theoretical equation may be adapted to empirical results. Empirical expressions may be reformulated in such a way that at very low concentration the Einsteinian equation \( \eta_r = 1 + k \cdot c \) is obtained, and/or that at finite concentrations viscosity becomes infinite.

A lot of formulas may be reduced to a power series, or a ratio of two power series. Other relations are of the semilogarithmical or exponential type, meaning a normal law distribution between some \( \eta_r \) and some \( c \) term. Such probability functions have been used in many other fields, e. g. reaction kinetics (first order reactions, temperature effects), crystal growth in time (1), relative humidity and moisture content (2). Log-normal distributions give a doubly logarithmical formula, popular in particle size distribution descriptions. Hyperbolic relations between \( \eta_r \) and \( c \) terms are often used, as has been done empirically for process-characterization, for liquid-vapour equilibria of binary systems, including azeotropes, especially by Waterman (3).

The formulas mostly contain several factors. The more important ones may be rubricated as follows. The varying symbols of the proposed relations will be transposed into this nomenclature.

- \( k \), a factor varying with the size, shape, rheological properties and orientation of the dispersed particles, being 2.5 for rigid spheres. Other elements, e. g. friction, may enter into /c factors used. \( k \) will as a rule appear in the numerator of \( \eta_r - c \) equations, in combination with a \( c \)-term. \( A, A_1, A_2, a_1, a_2 \) etc. constants for interaction between particles.

- \( s \), a factor of space filling, of sedimentation volume, a self crowding factor. \( 1/s \), a packing fraction, is the concentration of rheologically complete space packing. With a term \( (1 - s \cdot c) \) in the denominator of an equation, \( \eta_r \) will become infinite at \( c_{\text{max}} = 1/s \). In \( s \) must be included the interaction effect of the particles. Space filling for spheres and for non spherical particles may vary very considerably (4).

- \( n \), the power of one or more of the terms of the formulas. \( n \) may be connected with \( k \) or \( A \), or have the meaning of another interaction constant.

- \( h \), a hydration or solvatation factor. The real volume of the particles in the disperse system often is much higher than for the dry-state, and is the rheologically relevant one. Solvation itself may vary with the concentration.
c, concentration, in volume per unit of volume. For polymers often weight volume or weight fractions or % of dry substance are used. Apart from solvation, the effective density of polymers in solution may differ somewhat from that of the solid substance (5).

- \( \eta_0 \): viscosity of the continuous phase.
- \( \eta_s \): viscosity of solute or disperse phase.
- \( \eta_r \): viscosity of disperse system.
- \( \eta_{sp} = \eta_r - 1 \): specific viscosity.
- \( \eta_c = Z - \eta_{sp} = \frac{\eta_r - 1}{c} \): reduced (specific) viscosity.

Dispersed systems often are non-Newtonian, and then the viscosimetric data should be calculated in the right way from the measurements, which is not done always. There have been proposed nearly as much equations for the flow curve as for the concentration effect.

At higher shear rates the effects of laminar vortices in an annulus, and of turbulence generally must be reckoned with. The vortice effect may be smaller for suspensions. Turbulence may start prematurely in suspensions at some of the particles, compared with the medium alone. The movement of particles in turbulent flow is far less dependent on medium viscosity. In turbulent flow a suspension indeed may show a lower friction factor than the medium itself, be it liquid or gaseous. The behaviour of suspensions under vortical or turbulent conditions thus need not at all be similar to that of the medium. In turbulent flow there is a laminar zone of some tens of microns at a wall, and in a suspension there is an extra wall surface on account of the particles present.

The influence of shear rate \( D \) on the \( \eta_r - c \) relation will not be treated here, but \( D \)-effects are mentioned occasionally. Temperature effects will neither be discussed now.

Speaking about relative viscosity, the medium viscosity \( \eta_0 \) should be a constant. It is possible, that on mixing the two components, the viscosity of the continuous phase changes somewhat, by selective solubilization of the disperse phase or by selective adsorption on the particles from a non-uniform medium, which may decrease (6) or increase (7). \( \eta_0 \). More fundamental is the question whether the medium viscosity varies with the distance from the surface of a wall. Already Smoluchowski (8) supposed that adsorbed layers could be more viscous than the bulk of the medium. Henniker (9) reviewed phenomena and measurements, which show a deeper surface orientation, and suggest, that in liquids surface or wall layers of e.g. 0.01-0.1 \( \mu \) thickness have higher viscosity than the bulk, and may even be plastic, rigid and elastic. Broersma (10) developed a theory of non-uniform viscosity around particles. Weyl and Ormsby (11) discussed the importance of such (semi)-rigid medium layers, especially for water and clay or sand. The wall thickness e.g. of a capillary or particle, when below 1 \( \mu \), may influence too this immobilization effect. Such variations in the viscosity of the continuous phase will be more important for smaller particle sizes, below 0.1-0.5 \( \mu \), and will vary with the concentration of the dispersed phase. Interstitial liquid may behave otherwise than free bulk fluid. \( \eta_0 \) would not be a constant really. The absolute dimensions of the particles become important below a certain critical size, which will depend on the physical nature of the materials.

Medium viscosity sometimes is neglected totally, when network formation is taken as the only factor and hydrodynamical resistance to medium flow is not taken into account [Lodge (12, 13)]. The presence of surface films of a composition differing from the bulk liquid may make \( \eta_0 \) unimportant too. In these cases relative viscosity loses its significance and there can be spoken only of viscosity.

Some of the \( \eta_r - c \) equations will be presented in graphical form, using log \( \eta_r \) and \( c \). Some formulas will be tested on their suitability to represent the experimental results for suspensions of rigid spheres, which have been collected in another article to an average sphere curve, for sphere diameters between e.g. 0.3 and 400 \( \mu \) (14). Later on they will be judged for other particles. It is useful to linearize the equations and a graphical picture of such linear relations enables to check the validity and to determine the values of the factors in a formula.

### 1. Einsteinian formula

As an approximation of a more complex formula, Einstein (15, 16, 17) proposed, on hydrodynamical and diffusional grounds, for rigid uniform spheres moving without slip...